

PATENT SPECIFICATION

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(54) METHODS OF ELECTROLYSIS USING COMPLEX IRON OXIDE ELECTRODES

- (71) We, TDK ELECTRONICS COMPANY LIMITED, a Japanese Body Corporate of 14—6 Uchikanda 2-chome, Chiyoda-ku, Tokyo, Japan, do hereby declare:
- 5 the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- 10 This invention relates to methods of electrolysis.
- According to the invention there is provided a method of electrolysis which comprises using a sintered electrode having a spinel structure and the formula $M_xFe_{3-x}O_4$ (wherein M represents at least one of the metals Mn, Ni, Co, Mg, Cu, Zn and Cd, and x is from 0.05 to 0.5).
- 15 Electrodes of the hereinbefore specified spinel structure generally have good electrical and mechanical properties, and are preferably used as anodes, for example in the electrolysis of water or aqueous solutions of salts, for example sodium chloride. They can also be used as anodes in electropainting, electro-dialysis or electrophoresis, and furthermore they can be used as anodes in the electrolytic anti-corrosion treatment of metals.
- 20 Typically electrodes for use in accordance with the present invention can be prepared by sintering a mixture of from 60 to 95 mol % of Fe_2O_3 and from 5 to 40 mol % of a metal oxide of formula MO (wherein M is as hereinbefore defined). Alternatively, the metal oxide MO can be prepared *in situ* by sintering, for example using the corresponding metal carbonates or oxalates which decompose into the corresponding oxides on heating.
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In a particularly preferred method of producing electrodes for methods in accordance with the present invention, ferric oxide and the appropriate metal oxide, in a ratio of from 60 to 95 mol % to 40 to 5 mol % are mixed in a ball mill. The mixture is heated for 1 to 3 hours in air, at a temperature of from 800° to 1000°C. After cooling, the heated mixture is pulverized to obtain a fine powder having a particle size of less than 20 microns. The fine powder is formed into a shaped body, for example by compression moulding or slip casting. The shaped body is heated at a temperature of from 1100° to 1450°C in nitrogen or carbon dioxide containing at the most 5% by volume of oxygen. The heating or "sintering" is effected for a period from 1 to 5 hours and the shaped body is then slowly cooled in nitrogen or carbon dioxide containing at the most a small amount of oxygen.

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Electrodes produced using such a method have shown high corrosion resistance when used as anodes in the electrolysis of aqueous solutions containing chloride, nitrate or sulphate ions.

Electrodes having a relatively low resistivity (specific resistance) and poor corrosion resistance can result in the mixture which is sintered contains too low a percentage of metal oxide other than ferric oxide. However, electrodes having good corrosion resistance and a relatively high resistivity can be produced from mixtures containing high percentages of metal oxides other than ferric oxide. These electrodes can have resistivities of from 0.01 to 0.5 ohm. cm, and can be used at current densities of less than 50 Amp/dm² in aqueous solutions containing chloride,

nitrate or sulphate ions.

The following examples are given by way of illustration only:

Example 1.

As shown in Table 1.1, Fe_2O_3 and MnO were each weighed out to provide Samples Nos. 1—6 containing various molar percentages of Fe_2O_3 and MnO .

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TABLE 1.1

Sample No.	$\text{Fe}_2\text{O}_3 : \text{MnO}$ (mol %)	Fe_2O_3 (g)	MnO (g)
1	95 : 5	195.4	4.6
2	90 : 10	190.6	9.4
3	80 : 20	180.0	20.0
4	70 : 30	168.0	32.0
5	60 : 40	154.3	45.7
6	50 : 50	138.5	61.5

- 10 In each case the Fe_2O_3 and MnO were mixed in a ball mill for 20 hours. The mixtures were then pre-heated at a temperature of 800°C for about 3 hours and then cooled. The resulting mixtures were pulverized using an atomizer to obtain powders having a particle size of less than 20 microns. The powders were compression moulded at about 1 ton/cm² to form shaped bodies 110 mm \times 19 mm \times 5 mm. The shaped bodies were heated for 3 hours at a temperature of from 1200° to 1450°C in nitrogen containing less than 5% by volume of oxygen, and then slowly cooled in the same composition of atmosphere over a period of more than 10 hours to obtain electrodes.
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The resistivities of the electrodes (Nos. 1—6) obtained were measured by the four contact method. The values obtained are shown in Table 1.2. The electrodes were

then used as anodes in the electrolysis of an aqueous solution of sodium chloride (NaCl) under the following conditions. The corrosion resistance of each electrode (i.e. the anodes) was evaluated by measuring the loss in weight of each anode. The values obtained are shown as "corrosion loss" in Table 1.2.

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Conditions of electrolysis:

Concentration of NaCl : 0.5% by weight

Cathode Iron Plate: 100 mm \times 50 mm \times 0.2 mm

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Anode area: 0.25 dm²

Space between the electrodes: 5 cm

Voltage (D.C.): 10 V

Current density: 2 Amp/dm²

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Temperature of solution: $20 \pm 10^\circ\text{C}$

Duration of electrolysis: 50 hours

TABLE 1.2

Sample No.	Resistivity ($\Omega \cdot \text{cm}$)	Corrosion loss (mg/dm ³)
1	0.02	about 80
2	0.02	,, 40
3	0.01	,, 20
4	0.03	,, 20
5	0.09	,, 10
6	0.18	,, 10

In Figure 1 of the accompanying drawings, Curve 1a and 1b respectively show the variation of resistivity and corrosion loss with variations in the relative molar percentages of Fe_2O_3 and MnO.

In order to compare electrodes in accordance with the invention with a conventional magnetite electrode, an electrolysis was carried out under the same conditions as described above, except that a conventional magnetite was used as the anode in place of the electrode in accordance with the invention. The corrosion weight-loss of the magnetite electrode was 1140 mg/dm².

Commercially available magnetite electrodes generally contain additives such as SiO_2 or Al_2O_3 , to improve their mechanical properties. According to the composition, the magnetite electrodes give different resistivities and corrosion resistances. The resistivities are generally from 0.05 to 0.4 ohm. cm.

Example 2.

NiO was used in place of the MnO in Example 1. As shown in Table 2.1, Fe_2O_3 and NiO were each weighed out to provide Samples Nos. 7—12 having various molar percentages of Fe_2O_3 and NiO .

TABLE 2.1

Sample No.	$\text{Fe}_2\text{O}_3 : \text{NiO}$ (mol %)	Fe_2O_3 (g)	NiO (g)
7	95 : 5	195.2	4.8
8	90 : 10	190.1	9.9
9	80 : 20	179.1	20.9
10	70 : 30	166.6	33.4
11	60 : 40	152.5	47.5
12	50 : 50	136.3	63.7

Sintered electrodes in accordance with the invention were obtained by the procedure of Example 1.

The resistivities and corrosion resistance

of the electrodes (Nos. 7—12) obtained were measured and evaluated by the method in Example 1. The values obtained are shown in Table 2.2.

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TABLE 2.2

Sample No.	Resistivity ($\Omega \cdot \text{cm}$)	Corrosion loss (mg/dm ²)
7	0.01	about 90
8	0.01	,, 40
9	0.05	,, 20
10	0.05	,, 20
11	0.10	,, 20
12	0.30	,, 20

In Figure 2 of the accompanying drawings, Curves IIa and IIb respectively show the variation of resistivity and corrosion loss with variations in the relative molar percentage of Fe_2O_3 and NiO .

Example 3.

CoO was used in place of the MnO in Example 1. As shown in Table 3.1, Fe_2O_3 and CoO were each weighed out to provide Samples Nos. 13—18 having various molar percentages of Fe_2O_3 and CoO .

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TABLE 3.1

Sample No.	Fe ₂ O ₃ : CoO (mol %)	Fe ₂ O ₃ (g)	CoO (g)
13	95 : 5	195.2	4.8
14	90 : 10	190.1	9.9
15	80 : 20	179.0	21.0
16	70 : 30	166.5	33.5
17	60 : 40	152.3	47.7
18	50 : 50	136.1	63.9

Sintered electrodes in accordance with the invention were obtained by the procedure of Example 1.

5 The resistivities and corrosion resistances

of the sintered electrodes (Nos. 13—18) obtained were measured and evaluated by the method in Example 1. The values obtained are shown in Table 3.2.

TABLE 3.2

Sample No.	Resistivity (Ω.cm)	Corrosion loss (mg/dm ³)
13	0.02	about 96
14	0.02	.. 40
15	0.03	.. 40
16	0.06	.. 40
17	0.10	.. 40
18	0.16	.. 40

In Figure 3 of the accompanying drawing, Curves IIIa and IIIb respectively show the variation of resistivity and corrosion loss with variations in the relative molar percentage of Fe₂O₃ and CoO.

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Example 4.
MgO was used in place of the MnO in Example 1. As shown in Table 4.1, Fe₂O₃ and MgO were each weighed out to provide Samples Nos. 19—24 containing various molar percentages of Fe₂O₃ and MgO.

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TABLE 4.1

Sample No.	Fe ₂ O ₃ : MgO (mol %)	Fe ₂ O ₃ (g)	MgO (g)
19	95 : 5	197.4	2.6
20	90 : 10	194.5	5.5
21	80 : 20	188.1	11.9
22	70 : 30	180.5	19.5
23	60 : 40	171.2	28.2
24	50 : 50	159.7	40.3

Sintered electrodes in accordance with the invention were obtained by the procedure of Example 1.

The resistivities and corrosion resistances

of the sintered electrodes (Nos. 19—24) obtained were measured and evaluated by the method in Example 1. The values obtained are shown in Table 4.2.

TABLE 4.2

Sample No.	Resistivity ($\Omega \cdot \text{cm}$)	Corrosion loss (mg. dm^2)
19	0.03	about 40
20	0.05	.. 20
21	0.10	.. 20
22	0.17	.. 20
23	0.36	.. 30
24	8.35	.. 30

10 In Figure 4 of the accompanying drawings, Curves IVa and IVb respectively show the variation of resistivity and corrosion loss with variations in the relative molar percentage of Fe_2O_3 and MgO .

Example 5.

CuO was used in place of the MnO in Example 1. As shown in Table 5.1, Fe_2O_3 and CuO were each weighed out to provide Samples Nos. 25—30 containing various molar percentages of Fe_2O_3 and CuO .

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TABLE 5.1

Sample No.	$\text{Fe}_2\text{O}_3 : \text{CuO}$ (mol %)	Fe_2O_3 (g)	CuO (g)
25	95 : 5	194.9	5.1
26	90 : 10	189.5	10.5
27	80 : 20	177.8	22.2
28	70 : 30	164.8	35.2
29	60 : 40	150.1	49.9
30	50 : 50	133.5	66.5

25 Sintered electrodes in accordance with the invention were obtained by the procedure of Example 1 except that the shaped bodies were sintered at a temperature of from 1100° to 1350°C, instead of at a temperature of from 1200° to 1450°C.

The resistivities and corrosion resistances of the sintered electrodes (Nos. 25—30) obtained were measured and evaluated by the method in Example 1. The values obtained are shown in Table 5.2.

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TABLE 5.2

Sample No.	Resistivity ($\Omega \cdot \text{cm}$)	Corrosion loss (mg/dm^2)
25	0.10	about 110
26	0.07	.. 20
27	0.04	.. 20
28	0.20	.. 20
29	0.49	.. 20
30	40.70	.. 20

5 In Figure 5 of the accompanying drawings, Curves Va and Vb respectively show the variations of resistivity and corrosion loss with variations in the relative molar percentages of Fe_2O_3 and CuO .

Example 6.
ZnO was used in place of the MnO in Example 1. As shown in Table 6.1, Fe_2O_3 and ZnO were each weighed out to provide Samples Nos. 31—36 containing various molar percentages of Fe_2O_3 and ZnO.

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TABLE 6.1

Sample No.	$\text{Fe}_2\text{O}_3 : \text{ZnO}$ (mol %)	Fe_2O_3 (g)	ZnO (g)
31	95 : 5	194.8	5.2
32	90 : 10	189.3	10.7
33	80 : 20	167.4	22.6
34	70 : 30	164.2	35.8
35	60 : 40	149.3	50.7
36	50 : 50	132.5	67.5

15 Sintered electrodes in accordance with the invention were obtained by the procedure of Example 1.

The resistivities and the corrosion resis-

tances of the sintered electrodes (Nos. 31—36) obtained were measured and evaluated by the method in Example 1. The values obtained are shown in Table 6.2.

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TABLE 6.2

Sample No.	Resistivity ($\Omega \cdot \text{cm}$)	Corrosion loss (mg/dm^2)
31	0.03	about 110
32	0.04	.. 20
33	0.06	.. 20
34	0.09	.. 20
35	0.16	.. 20
36	0.35	.. 20

In Figure 6 of the accompanying drawings, Curves VI^d and VI^b respectively show the variation of resistivity and corrosion loss with variations in the relative molar percentages of 5 Fe_2O_3 and ZnO .

Example 7.

CuO and ZnO were used in place of the MnO in Example 1. As shown in Table 7.1, Fe_2O_3 , CuO and ZnO were each weighed out to provide Samples Nos. 37—39 containing various molar percentages of Fe_2O_3 , CuO and ZnO . 10

TABLE 7.1

Sample No.	Fe_2O_3 : CuO : ZnO (mol %)	Fe_2O_3 , (g)	CuO (g)	ZnO (g)
37	90 : 5 : 5	189.4	5.2	5.4
38	80 : 10 : 10	177.6	11.1	11.3
39	60 : 20 : 20	149.7	24.9	25.4

15 Sintered electrodes in accordance with the invention were obtained by the procedure of Example 1 except that the shaped bodies were sintered at a temperature of from 1150° to 1350°C in carbon dioxide containing less than 5% by volume of oxygen, in place of 20 sintering at a temperature of from 1200° to

1450°C in nitrogen containing less than 5% by volume of oxygen.

The resistivities and the corrosion resistances of the sintered electrodes (Nos. 37—39) obtained were measured and evaluated by the method in Example 1. The values obtained are shown in Table 7.2. 25

TABLE 7.2

Sample No.	Resistivity ($\Omega \cdot \text{cm}$)	Corrosion loss (mg/dm ²)
37	0.04	about 20
38	0.05	,, 20
39	0.40	,, 20

30 **Example 8.** NiO and CoO , NiO and ZnO , or NiO , CoO and ZnO were used in place of the MnO in Example 1. As shown in Table 8.1,

Fe_2O_3 , NiO , CoO and ZnO were each weighed out to provide Samples Nos. 40—43 containing various molar percentages of Fe_2O_3 , NiO , CoO and ZnO . 35

TABLE 8.1

Sample No.	Fe_2O_3 : NiO : CoO : ZnO (mol %)	Fe_2O_3 , (g)	NiO (g)	CoO (g)	ZnO (g)
40	80 : 10 : 10 : 0	179.0	10.5	10.5	0
41	90 : 5 : 0 : 5	189.7	4.9	0	5.4
42	91 : 3 : 3 : 3	190.9	2.9	3.0	3.2
43	82 : 6 : 6 : 6	180.9	6.2	6.2	6.7

40 Sintered electrodes in accordance with the invention were obtained by the procedure of Example 1.

The resistivities and the corrosion resis-

tances of the sintered electrodes (Nos. 40—43) obtained were measured and evaluated by the method in Example 1. The values obtained are shown in Table 8.2. 45

TABLE 8.2

Sample No.	Resistivity ($\Omega \cdot \text{cm}$)	Corrosion loss (mg dm^{-2})
40	0.09	about 30
41	0.07	,, 40
42	0.07	,, 40
43	0.18	,, 50

Example 9.

The procedure of Example 6 was repeated, except that CdO was used in place of the ZnO. Sintered electrodes having properties similar to those of Example 6 were obtained.

In order to reduce the electrical resistance of electrodes used in accordance with the present invention they can be produced in the shape of a hollow cylinder with one end closed and the inner surface coated with a layer of chemical plated or electro-deposited metal such as copper or nickel.

WHAT WE CLAIM IS:—

1. A method of electrolysis which comprises using a sintered electrode having a spinel structure and the formula $M_xFe_{3-x}O_4$ (wherein M represents at least one of the

metals Mn, Ni, Co, Mg, Cu, Zn and Cd, and x is from 0.05 to 0.5).

2. A method according to claim 1, wherein M represents only one of the said metals.

3. A method according to either of the preceding claims, wherein the electrode has a resistivity of from 0.01 to 0.5 ohm.cm.

4. A method according to claim 1, substantially as herein described.

5. A method according to claim 1, substantially as herein described with reference to any one of the Examples.

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FIG. 1

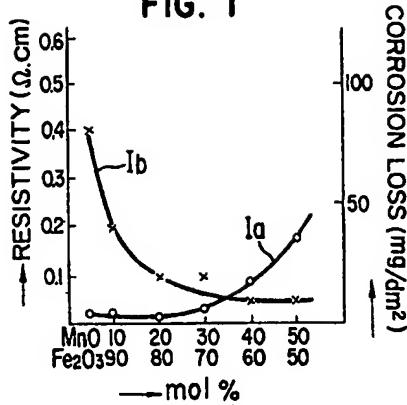


FIG. 2

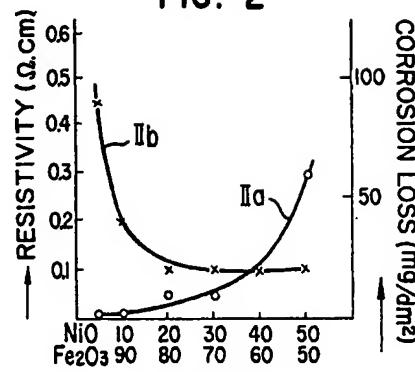


FIG. 3

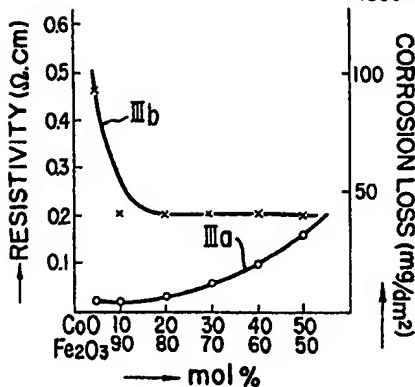


FIG. 4

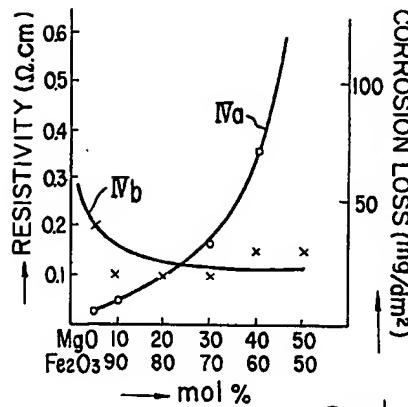


FIG. 5

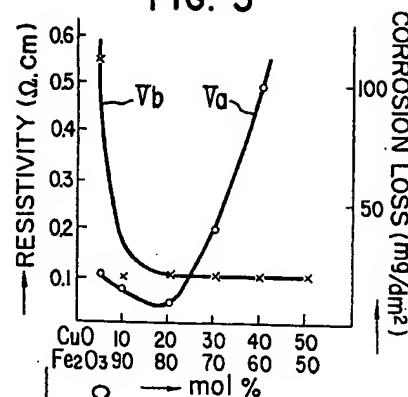


FIG. 6

